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Abstract

A novel redox active organic/inorganic hybrid composite material is prepared by oxidative intercalation of 2,5-dimercapto-1,3,4-thiadiazole (DMcT) or its disulfide dimer into a V_2O_5 xerogel. X-ray diffraction shows a change in the layer spacing between that of the parent V_2O_5 material (11.55 Å) and that of the new intercalation material (13.5 Å). This change is consistent with loss of some interstitial water during intercalation of the disulfide polymer of DMcT. Elemental analysis gives a composition for the intercalation material of [(polyDMcT)$_{0.25}$•V_2O_5•1.4H$_2$O]. The cyclic voltammetry and galvanostatic discharge behavior of the parent V_2O_5 xerogel and the new intercalation material are directly compared. The [(polyDMcT)$_{0.25}$•V_2O_5•1.4H$_2$O] hybrid composite material is shown to have superior discharge behavior, making it an attractive candidate material for use as a cathode in lithium secondary batteries.

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The cathode behavior in lithium secondary batteries comprises a significant weakness in their overall performance[1-9]. Recent work in this area has focused on redox active metal oxides or chalcogenides that are capable of forming intercalation compounds with Li^+. A key motivation in the search for new cathode materials is the desire to increase the rates at which Li^+ transport occurs such intercalation materials, since this rate is often limiting with respect to the overall process of cathode reduction [6-9].

A common strategy to increase cathode reduction rates involves the use of cathode materials with very small particle sizes (and consequently high surface areas), because this reduces the average distance over which Li^+ must diffuse through the host material [6-9]. Another approach that does not appear to have been previously investigated is to attempt to increase Li^+ transport rates by manipulating the interlayer spacing. This might be achieved by intercalation of a variety of intercalants, since this is known to increase the interlayer spacing.[4,10-27] Examples of intercalants include thiophene, pyrrole and aniline, all of which are known to oxidatively polymerize when intercalated into highly oxidizing layered materials such as V_2O_5.[25,26,28-34] However, in such a case, it would be necessary to achieve intercalation densities that are less than maximal, since filling the interlayer region with intercalants would likely lead to steric congestion that would actually reduce Li^+ transport rates. Previous work on intercalation has focused on the generation of novel optical or electronic properties.[25,26,28-31] However, little has been done on the influence of intercalants on the redox properties of layered compounds, especially with respect to their influence on Li^+ transport rates.

When choosing the intercalant in such an approach, several factors must be considered. For example, it is highly desirable that the intercalant exhibit a reversible redox process in the same potential range as that for the host material, and that it have an

intrinsically high energy density. Thus, the energy density of the resulting composite material should not be reduced excessively by the presence of the intercalant, and may, in fact, be enhanced. It is also desirable that the intercalant become negatively charged during reduction, since this allows electrostatic accommodation of Li^+ generated at the anode during discharge. One compound that meets these criteria is 2,5-dimercapto-1,3,4-thiadiazole, DMcT (Scheme 1). This compound has been extensively investigated due to reports that mixtures of it with polyaniline exhibit high energy density and highly reversible charge-discharge behavior.[37-43] In this communication, we show that this compound can be intercalated into V_2O_5 xerogels to produce a new cathode material that has considerably enhanced redox properties compared to the parent material.

An important concern with DMcT and related compounds with sulfur-based (thiolate/disulfide) redox couples is that, while they have very attractive thermodynamic properties for application as cathode materials (i.e. fairly positive redox potential and low mass per electron), they do not have similarly attractive kinetic properties. Specifically, they tend to have very low rates of electron transfer[35,36] and also to suffer from complications related to the polymerization and depolymerization processes that occur during the redox event.[45,46] In the case of the DMcT/polyaniline composite material, a detailed electrochemical study of a related thiol/disulfide model system (2-mercapto-5-methyl-1,3,4-thiadiazole) has suggested that the redox process is facilitated by proton transfer between polyaniline and DMcT.[39,44-46] These results imply that use of materials such as DMcT will require catalysis or facilitation of the redox process to achieve acceptable rates. It is significant in this regard that several transition metal systems have been shown to catalyze thiol/disulfide redox processes.[47-58]

Choice of an appropriate host material requires consideration of many of the same factors that were discussed above. A considerable body of work exists that reveals the

relative behavior of a variety of candidate materials.[14-27] The best of these include the cobalt oxides, manganese oxides and vanadium oxides.[14-16,23-25,27] In particular, V_2O_5 xerogels have been reported to have excellent properties, due predominantly to very high intrinsic surface area[6-9,59-62]. Based on its superior properties and relative ease of preparation, we have used this material in the current study.

The V_2O_5 xerogel solution was prepared as previously described[63,64] by ion exchange of $NaVO_3$ to produce HVO_3 followed by aging for at least two weeks. Xerogel films were prepared by simple solvent casting and drying under vacuum at room temperature for 40 hours. These films are flexible and have a deep wine red color. X-ray diffraction (Figure 1)[65] gives an interlayer spacing of 11.55 Å, consistent with previous reports for this material[63,64]. The films are essentially insoluble in common organic solvents, such as acetone, acetonitrile (AN), propylene carbonate and chloroform, but swell and ultimately dissolve in water. Initially, DMcT intercalation was achieved by immersing the film for 20 hours in a 33 mM solution of DMcT in a 20:80 (v/v %) mixture of AN/water. This results in a color change to a deep bluish-green due to vanadium reduction during the oxidative intercalation of DMcT. The films formed in this way can be removed from the substrate to give free-standing films. Elemental analysis of the resulting material[66] gives a composition of $(polyDMcT)_{0.25} \cdot V_2O_5 \cdot 1.4H_2O$. XRD revealed that the layered nature of the V_2O_5 matrix in this material was preserved, and seven (00l) reflections were observed corresponding to a new interlayer spacing of 13.5Å (Figure 1). This value is consistent with expectations for intercalation of organic molecules into vanadium oxide.[25,28,30,31] The ca. 2 Å net layer expansion represents the removal of one water layer (ca.2.8Å) from the intralamellar space during the insertion of the DMcT polymer (Scheme 2).[25,63,64] IR spectroscopy revealed that the product of DMcT intercalation was the oxidized disulfide polymer, which has prominent bands at 1382 and 1046 cm^{-1}.[67]

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Initial electrochemical experiments with V_2O_5/DMcT mixtures were not satisfactory. Electrodes prepared from these compounds exhibited very low charge recoveries and distorted voltammetry indicative of high resistivity. We speculated that this is due to the strongly acidic nature of DMcT (pK_a = -1.36)[44] which may influence the mesoscopic structure of the xerogel material. To circumvent this problem, the intercalant was changed to the disulfide dimer of DMcT (Scheme 1). This compound is much less acidic than DMcT, as demonstrated by the fact that it is not deprotonated by pyridine in AN solutions.[44] For electrochemical experiments, samples of the parent xerogel and the V_2O_5/DMcT dimer intercalation material were prepared in the following ways, respectively. V_2O_5 xerogel solution (containing 20 mg or 1.1 x 10^{-4} mol of V_2O_5) was mixed with 100 mg of carbon powder (Ultra "F" grade), and then ca. 20 mg of the mixture was spread on a Pt mesh electrode (52 mesh, 10 mm x 7 mm). V_2O_5 xerogel solution (containing 7.3 mg or 4.01 x 10^{-5} mol of V_2O_5) was mixed with 12.7 mg (4.26 x 10^{-5} mol) of solid DMcT dimer and 100 mg of carbon powder (Ultra "F" grade), and then ca. 20 mg of the mixture was spread on a Pt mesh electrode (52 mesh, 10 mm x 7 mm). Since V_2O_5 xerogel acts as a good binder, it was not necessary to add other binders. After vacuum drying at room temperature, a Pt mesh electrode that had ca. 18 mg of active material was obtained in each case. For purposes of comparison, the theoretical capacities for these two electrodes were calculated assuming a V^{5+} to V^{3+} transition for V_2O_5[7-9] and a redox process with 2 e per ring for the DMcT dimer[37-46]. These charges are 7.08 C and 5.32 C, respectively. Figure 2 shows the electrochemistry of both the parent xerogel (dashed) and the intercalation material (solid). The intercalated material shows new symmetrical redox peaks at ca.-0.15 V (oxidation) and ca.-0.65 V (reduction), as well as a higher charge, in spite of the smaller capacity expected for the intercalation electrode.

Galvanostatic discharge experiments were used to compare the discharge behavior of this new material to that of the parent xerogel. In these experiments, two samples with very similar theoretical capacities were charged for 10 min at a potential of +1.4 V. Then, a reductive current was imposed on the sample while the potential was monitored. This was repeated at several currents. As can be seen in Figure 3, voltage plateaus are observed that are less positive with increasing current density. Significantly, the V_2O_5/DMcT dimer intercalation material shows more positive voltage plateaus at each applied current density than those of the parent xerogel, indicating much better discharge behavior than that of the parent V_2O_5 material. The differences are largest at higher current densities, where kinetic limitations are expected to be most evident.

It can be concluded from these results that the discharge performance of V_2O_5 is improved by intercalation of the organosulfur compounds used here. This promising result suggests that the arguments presented above regarding the influence of layer expansion on transport rates for Li^+ may, indeed, pertain to these materials. The issue of whether the thiol/disulfide redox process is catalyzed or otherwise facilitated by the V_2O_5 material remains unresolved. We are currently exploring several experimental avenues to determine the root of the improved behavior in these materials, and to explore the generality of these findings.

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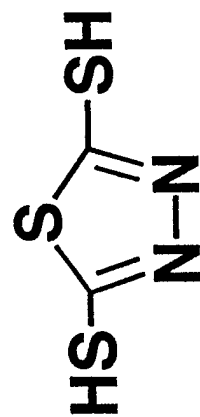
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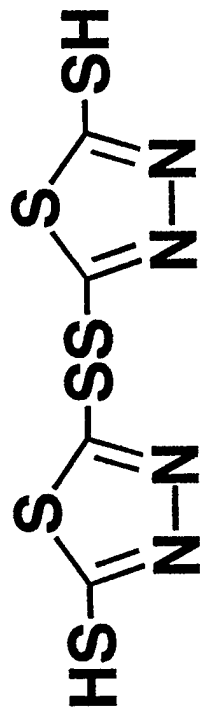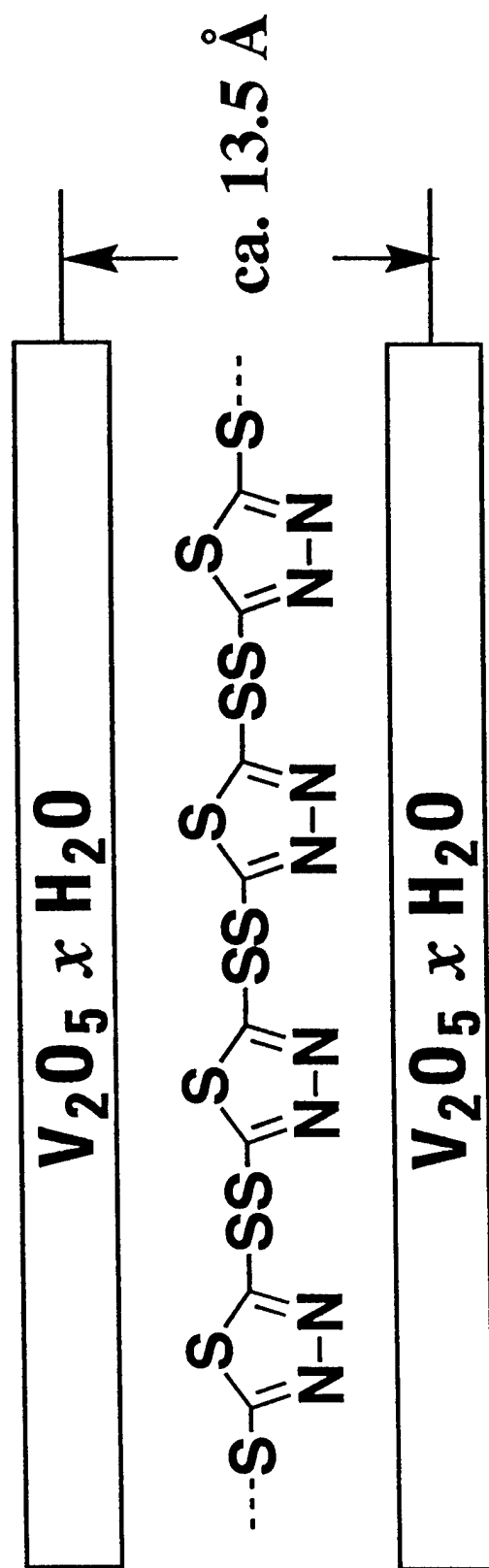
DMcT

Legend of Figures

Figure 1 X-ray powder diffraction pattern of the parent V_2O_5 material (upper) and of the (polyDMcT)$_{0.25}$•V_2O_5•$1.4H_2O$ composite material (lower).

Figure 2 Cyclic voltammograms for a) V_2O_5 xerogel/DMcT dimer, and b) V_2O_5 xerogel alone in 0.2 M LiClO$_4$ AN solution. Scan rate : 5 mV/s. T = 25°C.

Figure 3 Galvanostatic discharge curves for V_2O_5 xerogel/DMcT dimer (solid) and V_2O_5 xerogel (dashed) at various current densities in 0.2 M LiClO$_4$ AN solution.

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Figure 2

E / V vs. Ag/AgCl

-1.0 -0.8 -0.6 -0.4 -0.2 0.0 0.2 0.4 0.6 0.8 1.0 1.2 1.4

1 mA

(a)

(b)

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Figure 3